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INFLUENCE OF CURE SYSTEMS ON DIELECTRIC AND VISCOELASTIC RELAXATIONS IN
CROSSLINKED CHLOROBUTYL RUBBER

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INTRODUCTION

Dielectric spectroscopy has been used as a probe of molecular behavior in organic molecules for a number of years.^{1, 2} In conjunction with dynamic mechanical spectroscopy, it has been used to correlate the dynamic mechanical and dielectric relaxation behavior of a number of polymer systems, as well as providing insight into the molecular structural factors responsible for multiple relaxation mechanisms in polymers.

In many instances where simultaneous measurements of dynamic mechanical and dielectric behavior were performed,³⁻⁶ the polymers involved were comparatively simple systems. Although synthetic rubbers have been extensively characterized by dynamic mechanical measurements, fewer dielectric studies have been performed on these systems.⁸⁻⁹ In a recent work⁸, we showed that the dielectric behavior of filled chlorobutyl and butyl rubber was significantly influenced by carbon black particle size, type, and loading. Results obtained on unfilled systems indicated that the principal dielectric relaxation was a cooperative process involving molecular motion of chain segments coupled with thermally activated rotation of polar crosslinking molecules. It was also shown that the dielectric behavior followed the Kolrausch-Williams-Watts (KWW) "stretched exponential" function, which has recently received great interest as a sort of "universal relaxation" function, with applicability to a large number of physical systems.¹⁰⁻¹³ In the present work, we have extended our study to compare the dielectric and viscoelastic behavior of chlorobutyl rubber (CIIR) cured only with zinc oxide, and with increasingly complex cure systems, as well as varying plasticizer loadings. For comparison purposes, we have also included the structurally related butyl rubber (IIR), which does not possess molecular dipoles due to chlorine atoms. The similarity between the observed

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viscoelastic behavior and dielectric behavior is discussed in terms of molecular motions.

EXPERIMENTAL

The polymer systems studied are summarized in Table 1. Compounded rubber samples were obtained from the Burke Rubber Company of San Jose, CA. Proper cure conditions were determined with a Monsanto oscillating disc rheometer as per ASTM D2084.

Experimental samples were compression molded at 155 degrees C. Dynamic mechanical and dielectric measurements were performed as previously described.⁶ Tensile measurements were performed as per ASTM D412.

Table 1. Formulations for IIR and CIIR Rubbers

System	IIR	CIIR
<u>Component (Parts per Hundred of Rubber (P.H.R.))</u>		
Exxon Butyl 268	100.0	
Chlorobutyl HT1066		100.0
Zinc Oxide	5.0	5.0
Schenectady SP1055*	12.0	0-8.0
MBTS**		0-2.0
Stearic Acid	1.0	1.0
Diphenyl guanidine		0-0.5
Sunpar 120***	0-10.0	0-10.0

* Brominated methylol phenol resin

** 2, 2'-Benzothiazyl disulfide

*** Paraffinic oil

RESULTS

Dynamic Mechanical Behavior.

Fig. 1 shows the isochronal, temperature-dependent storage Young's modulus and loss tangent, obtained with a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA), for three different cure systems in the chlorobutyl rubber. One primary transition is clearly evident in the loss tangent, with a secondary shoulder that has been classified by others¹⁴ in the analogous bromobutyl as a β transition due to the rotation of pendant methyl groups. Similar behavior was observed for the butyl rubber. It can be seen that the increased crosslinking in the chlorobutyl rubber causes an increase in the storage modulus, a slight decrease in the peak magnitude of $\tan \delta$, and a shift upward in the temperature at which the maximum of $\tan \delta$ occurs.

These trends are mirrored in the extended master frequency curves constructed by time-temperature superposition using measurements from the transfer function technique.⁶ Fig. 2 shows master frequency curves for two different cure systems. All of the materials tested behaved as thermorheologically simple materials, and could be shifted equally well by either an Arrhenius shift function, or standard WLF form. Note that, although the $\tan \delta$ scale is a linear one, the apparent superposition is good. The shoulder seen in the DMTA scans appears to manifest itself as a shoulder on the high frequency side of the $\tan \delta$ curve in the master frequency curves, at approximately 100 kHz. This is interpreted as a

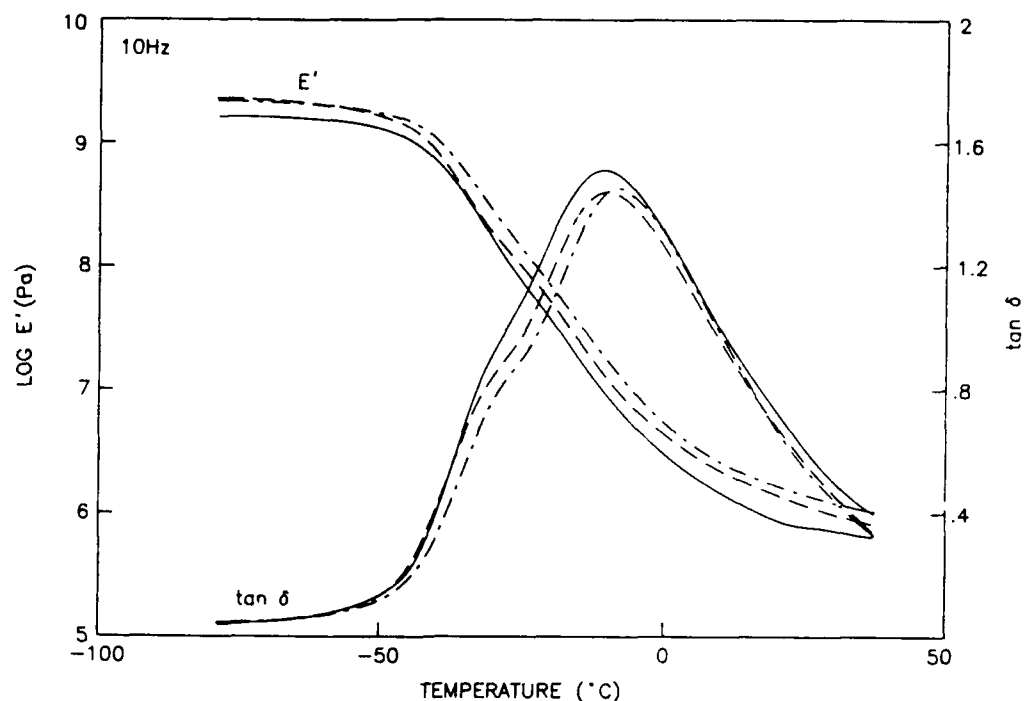


Fig. 1. Plot of storage Young's modulus and loss tangent for chlorobutyl rubber as a function of temperature at 10 Hz: solid lines, 5 phr of ZnO; dashed lines, 5 phr ZnO and 6 phr SP1055; double dashed lines, 5 phr ZnO, 6 phr SP1055, 2 phr MBTS, 0.5 phr DPG.

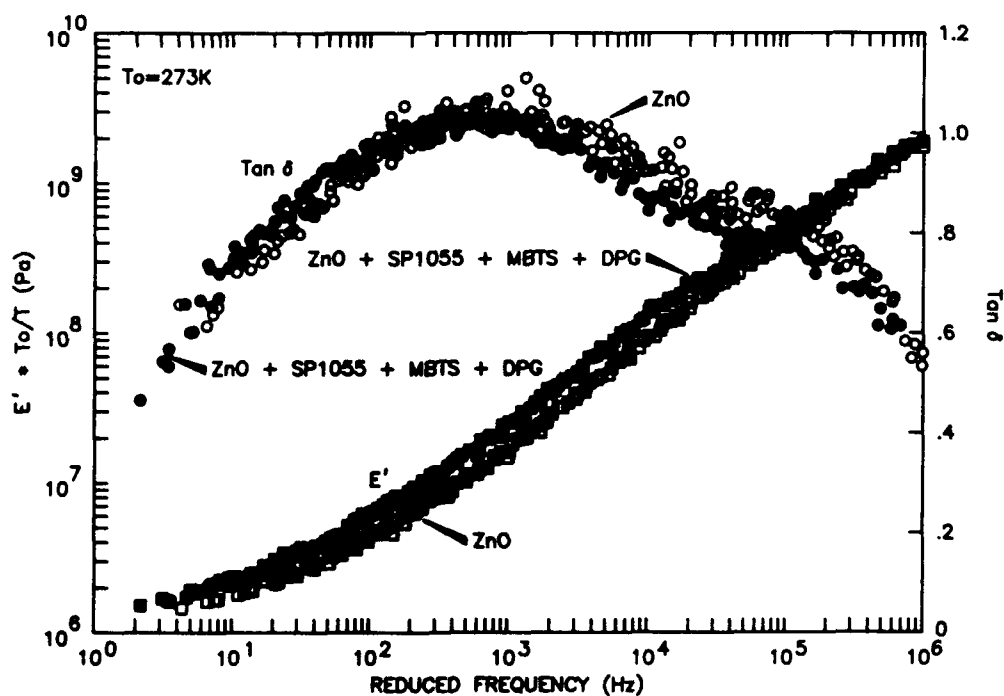


Fig. 2. Plot of storage Young's modulus and loss tangent as a function of reduced frequency for chlorobutyl rubber with two different cure systems at a reference temperature of 273.15 K: clear squares and circles, 5 phr of ZnO; solid squares and circles, 5 phr ZnO, 6 phr SP1055, 2 phr MBTS, 0.5 phr DPG.

coupling of the α and β processes in the primary glass-to-rubber viscoelastic relaxation.

Addition of nonpolar plasticizer at a constant level of crosslinking had the expected effects in both the butyl and chlorobutyl rubbers. The increased free volume led to a decrease in the storage modulus, a lowering of the temperature of maximum $\tan \delta$, and increase in the maximum of $\tan \delta$. This is shown for the butyl rubber in Fig. 3. The chlorobutyl rubber showed similar effects.

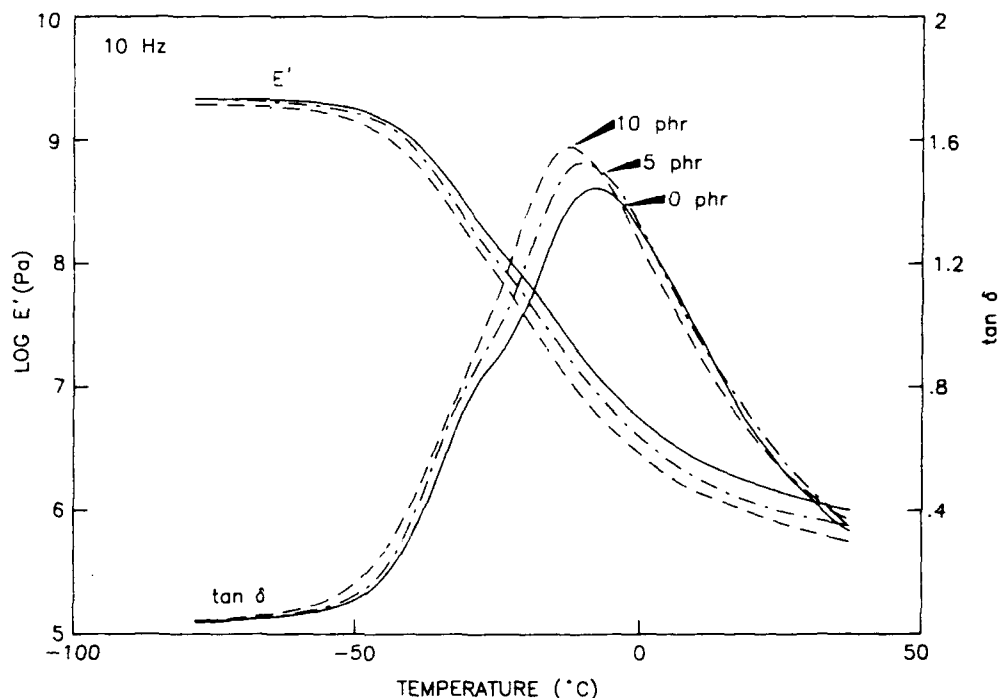


Fig. 3. Plot of storage Young's modulus and loss tangent for plasticized butyl rubber as a function of temperature at 10 Hz: solid lines, 0 phr of Sunpar 120; double dashed lines, 5 phr Sunpar 120; dashed lines, 10 phr Sunpar 120.

The KWW function has been used as a fitting function for both mechanical relaxations and dielectric spectra. Roland and Ngai¹² recently applied the KWW function to the glass transition dispersion of the dynamic mechanical spectrum of polybutadiene-polyisoprene blends. Muzea, Perez, and Johari recently described its application¹³ to the shear modulus and loss spectrum of the β -relaxation of poly(methyl methacrylate). This was the approach used to fit the dynamic mechanical spectra of the chlorobutyl rubber samples to the KWW function.

Two different methods were used to examine the glass transition dispersion region for purposes of fitting to the KWW function. The first used the step-isotherm mode of a Polymer Laboratories DMTA to measure the Young's loss modulus at ten different frequencies from 0.1 to 30 Hz, at temperatures near the glass transition. This resulted in a relatively narrow isothermal frequency spectrum, and considerable scatter in KWW fits. The second approach used the transfer function technique and time temperature superposition to construct extended master frequency curves at a reference temperature of 243.15 K, so that the dispersion curve in the loss modulus covered approximately the same frequency range as the

dielectric loss. These were then considered to represent isothermal frequency curves at the reference temperature. An example of such a curve is shown in Fig. 4. A third order polynomial was used to find the maximum in the loss modulus and frequency of maximum loss before fitting these to the KWW function.

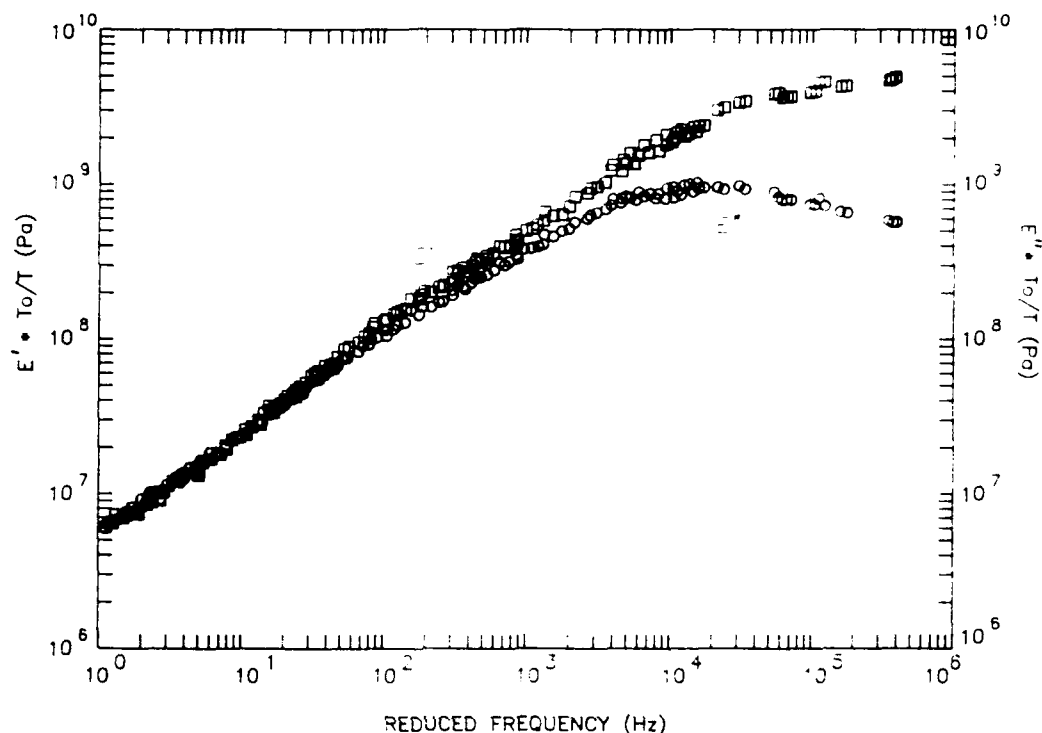


Fig. 4. Reduced frequency curve of Young's storage and loss moduli for chlorobutyl rubber cured with 5 phr ZnO, 3 phr SP1055, MBTS, and DPG. $T_0 = 243.15$ K.

Figs. 5 and 6 show the normalized dynamic mechanical spectra for one material, and the resultant fit to the KWW function using an exponent of 0.475. This is the chlorobutyl rubber with the most complex cure system, using ZnO, SP1055, MBTS, and DPG. In contrast, chlorobutyl rubbers cured with ZnO alone, and ZnO combined with SP1055, were fitted to the KWW function with an exponential factor of 0.375. This indicates a broader distribution of relaxation times in the dynamic mechanical behavior of the rubbers with the simpler cure systems.

Dielectric Behavior

The dielectric behavior of the chlorobutyl rubber was significantly affected by the crosslinking system used. Relative permittivities were low for the systems, on the order of 2.7, and showed little frequency dependence. Fig. 7 shows the dielectric loss for four different cure systems, plotted as a function of frequency at 295.15 degrees K. In all cases, a secondary maximum is seen at approximately 22-25 kHz. The exact nature of this peak is not clear. It was also observed in the butyl rubbers, but not in other polymers with higher losses, such as peroxide cured acrylonitrile rubber, and sulfur cured natural rubber. It did not show any frequency shift as a function of temperature, indicating that it is probably an instrumental artifact, and not a separate transition.

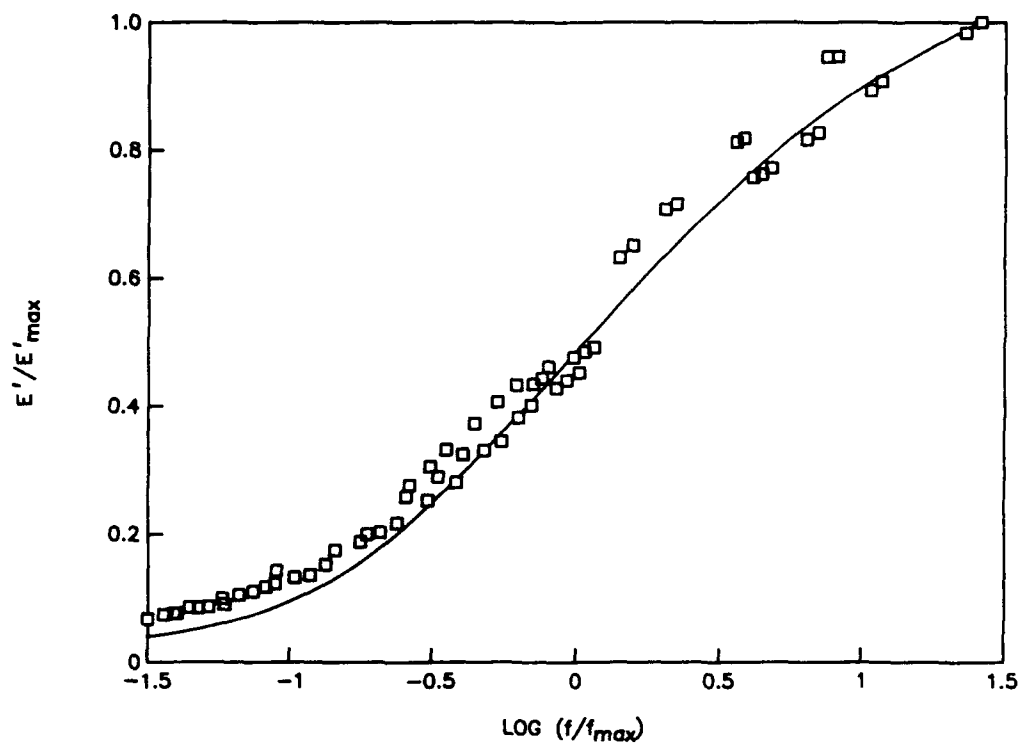


Fig. 5. Plot of normalized Young's storage modulus versus normalized frequency for chlorobutyl rubber at $T_0 = 243.15$ K. Line represents fit from KWW function with $\beta = 0.475$.

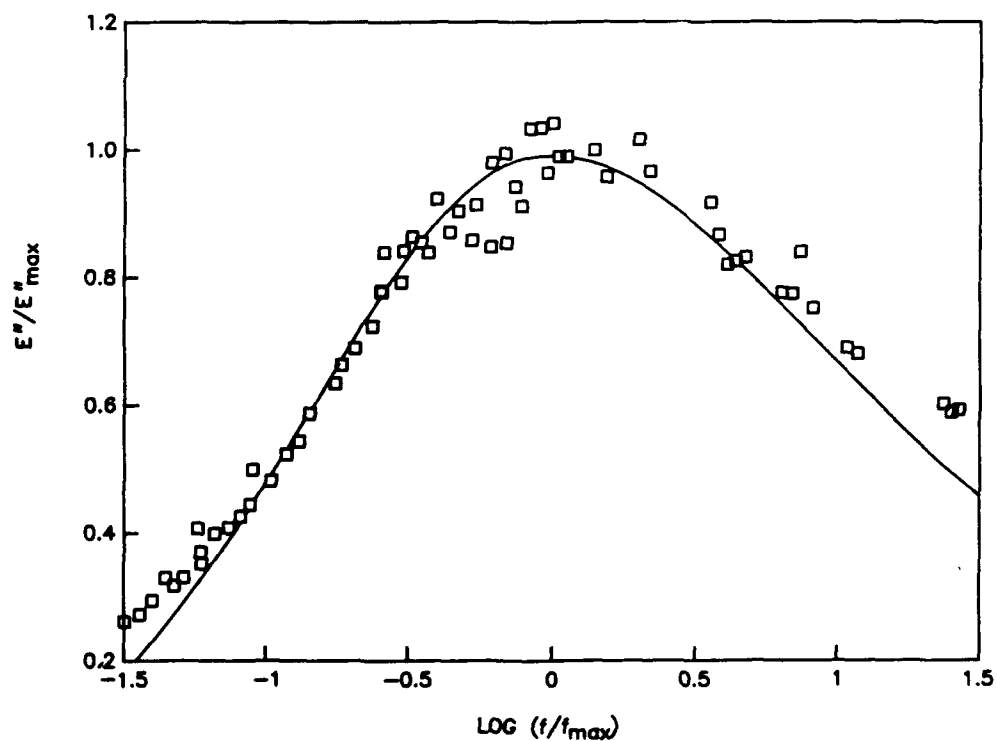


Fig. 6. Plot of normalized Young's loss modulus versus normalized frequency for chlorobutyl rubber at $T_0 = 243.15$ K. Line represents fit from KWW function with $\beta = 0.475$.

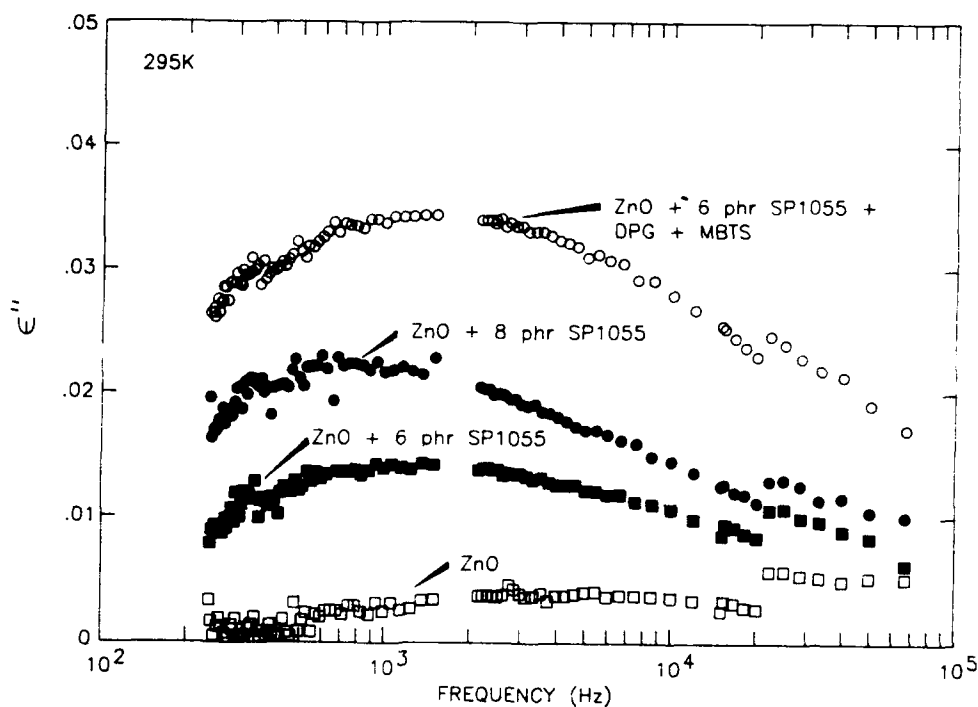


Fig. 7. Plot of dielectric loss as a function of frequency at 295.15 K for chlorobutyl rubber: clear squares, cured with 5 phr ZnO; solid squares, 5 phr ZnO and 6 phr SP1055; solid circles, 5 phr ZnO and 8 phr SP1055; clear circles, 5 phr ZnO, 6 phr SP1055, 2 phr MBTS, 0.5 phr DPG.

The effects of different cure systems upon dielectric relaxation behavior can be more clearly seen in Fig. 8, where the dielectric loss is plotted as a function of temperature at a reference frequency of 1000 Hz. The systems that use the brominated methylol phenol resin, SP1055, show relatively strong maxima in the range of room temperature, although some weaker frequency dependent dispersion is still present at lower temperatures. This is consistent with the primary mechanism of charge conduction in these materials being due to polar materials used in the crosslinking system.

Plots of $\log f_{\max}$ versus $1/T$ were linear for the systems using brominated methylol phenol resin cures, indicative of a thermally activated process. An example of this is shown in Fig. 9, which depicts relaxation maps for a butyl and two different chlorobutyl rubber compounds. The range of $\log f_{\max}$ versus $1/T$ values that could be plotted was limited by the fact that the peak of the dielectric loss tended to drop below the lowest frequency at which reliable measurements could be achieved as the temperature was lowered. It was found that the dielectric spectra taken at different temperatures could be superimposed reasonably well in a master curve of $\epsilon''/\epsilon''_{\max}$ versus $\log (f/f_{\max})$, when the portion of the transition considered to be alpha in character was considered (Fig. 10).

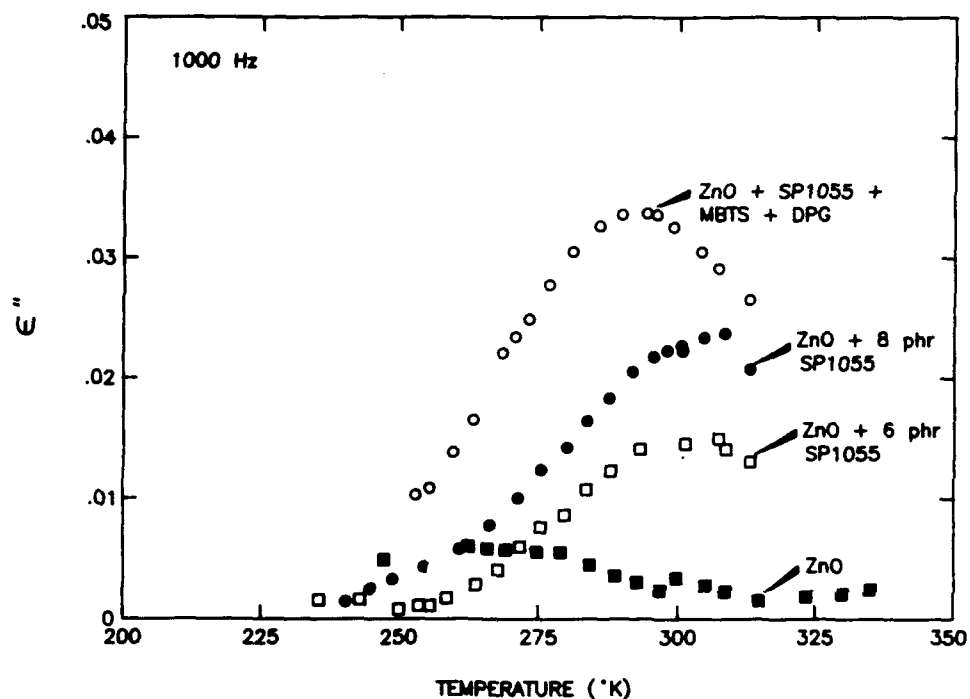


Fig. 8. Plot of dielectric loss as a function of temperature at 1000 Hz for chlorobutyl rubber: solid squares, cured with 5 phr ZnO; clear squares, 5 phr ZnO and 6 phr SP1055; solid circles, 5 phr ZnO and 8 phr SP1055; clear circles, 5 phr ZnO, 6 phr SP1055, 2 phr MBTS, 0.5 phr DPG.

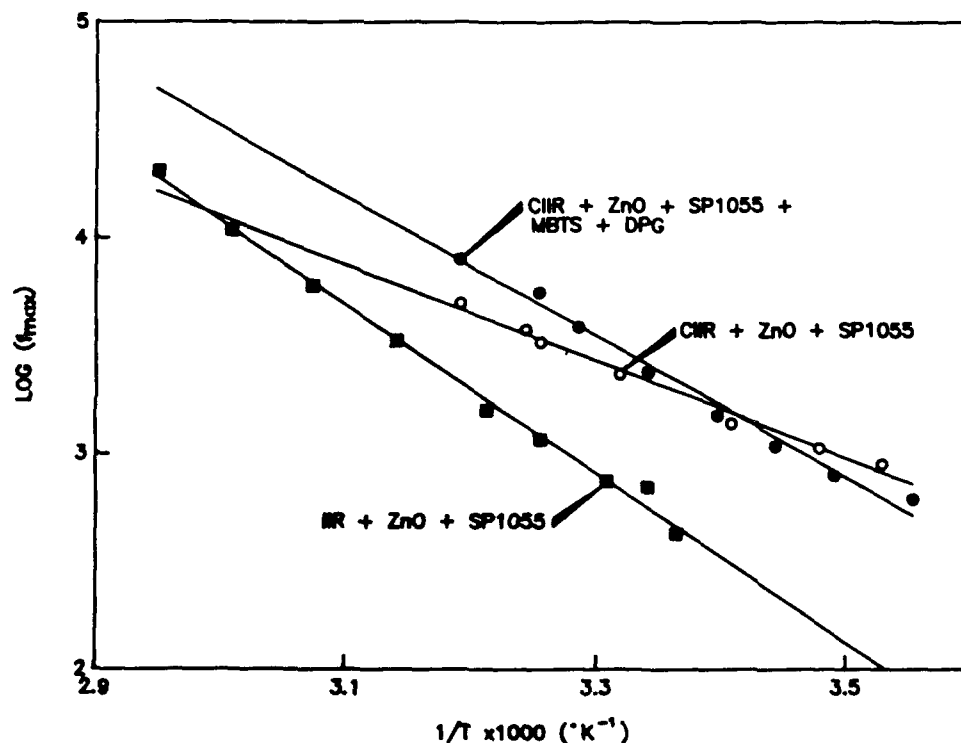


Fig. 9. Relaxation maps for butyl rubber and chlorobutyl rubber with two different cure systems.

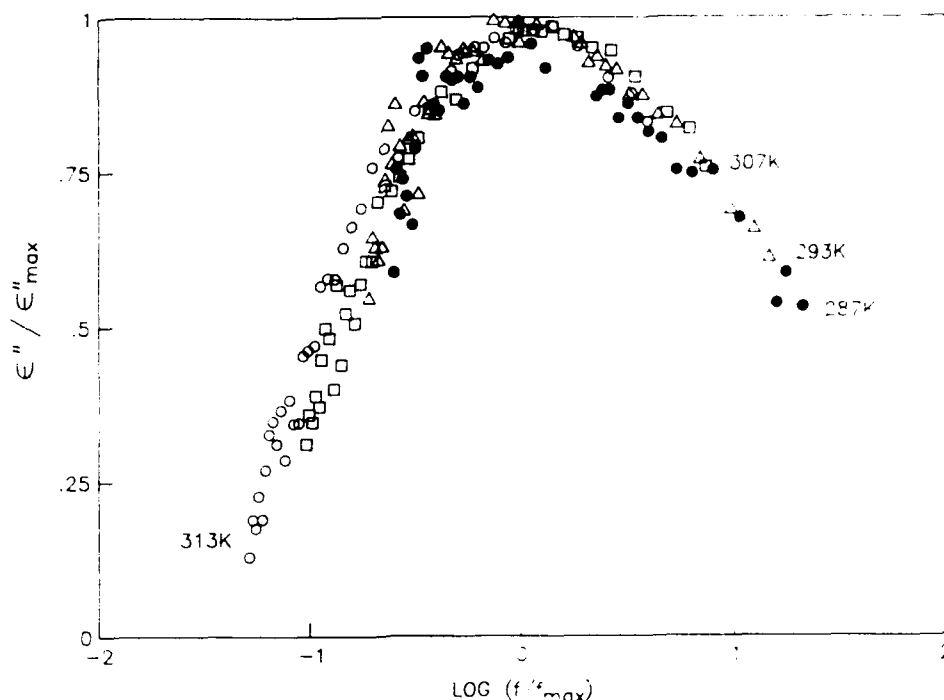


Fig. 10. Master curve of normalized dielectric loss versus f/f_{\max} for chlorobutyl rubber cured with 5 phr ZnO and 6 phr SP1055 resin: open circle, 313K; open square, 307K; open triangle, 293K; and solid circle, 287K.

Addition of plasticizer showed an effect upon the dielectric relaxation, in both the butyl and chlorobutyl systems, that was analogous to the dynamic mechanical relaxation when plotted as a function of temperature at a fixed frequency. The maximum in the dielectric loss increased, and showed slight temperature shifts, as shown in Fig. 11.

The dielectric behavior of the systems could be fitted reasonably well using the KWW function. This was done using both the tables of Moynihan, Boesch, and Laberge¹⁵, and a slight modification of the method of Weiss, Bendler, and Dishon (WBD)¹⁶. These authors define the dielectric loss function as

$$\epsilon'' = A z Q_{\beta}(z) \quad (1)$$

where $z = \omega\tau$, β is the exponential factor (called α_{β} by WBD), τ is the relaxation time in the KWW function $\phi(t) = \exp -(t/\tau)^{\beta}$, $\omega = 2\pi f$, with

$$Q_{\beta}(z) = \left(\frac{1}{\Gamma(\beta)}\right) \int_0^{\infty} e^{-u^{\beta}} \cos(zu) du, \quad (2)$$

and

$$A = \epsilon_0 - \epsilon_{\infty} \quad (3)$$

The peak of the loss data was first fitted with a third order polynomial to locate the peak position and height. The values of τ and A were then determined by using the approximations found in Ref. 16. This information was used, along with approximations for Q_β given in Ref. 17, to calculate the loss values for a given combination of beta and frequency. Brent's method¹⁸ was employed to determine the value of beta iteratively by minimizing the value of the difference function

$$D(\beta) = \sum_{\omega=\omega_{\min}}^{\omega=\omega_{\max}} \left(\epsilon''(\omega)_{\text{calc}} - \epsilon''(\omega)_{\text{data}} \right)^2 \quad (4).$$

The two methods gave good agreement. An example of the type of fit obtained is shown in Fig. 12. The fit was found to be better for certain materials and at certain temperatures than for others. All of the materials showed values of the fit factor, β , in the neighborhood of 0.4, as has been observed for many other types of polymers. The value of β also tended to vary somewhat with temperature. In comparing different chlorobutyl rubbers, those with the more complex crosslinking systems had a greater temperature dependence of β (Fig. 13). The KWW fits were not done at all temperatures for these materials, due to the fact that the loss tended to decrease in magnitude and shift to lower frequencies as the temperature was lowered. The entire transition region was therefore not covered at lower temperatures. The low temperature dielectric spectra of the zinc oxide cured rubber could be fitted to the KWW function, with a β value of 0.375.

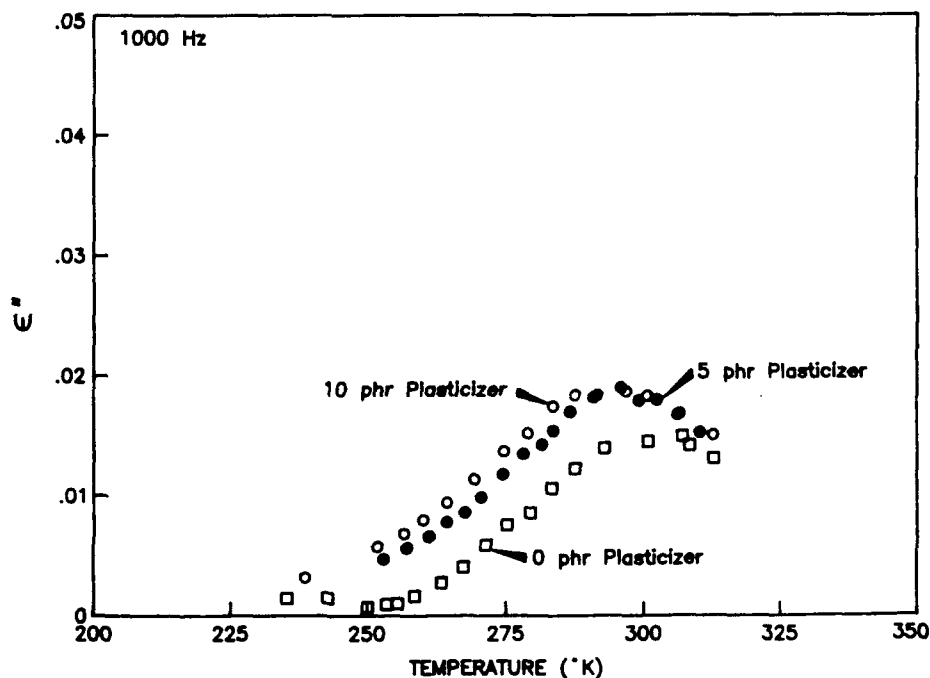


Fig. 11. Plot of dielectric loss as a function of temperature for chlorobutyl rubber with varying plasticizer loadings.

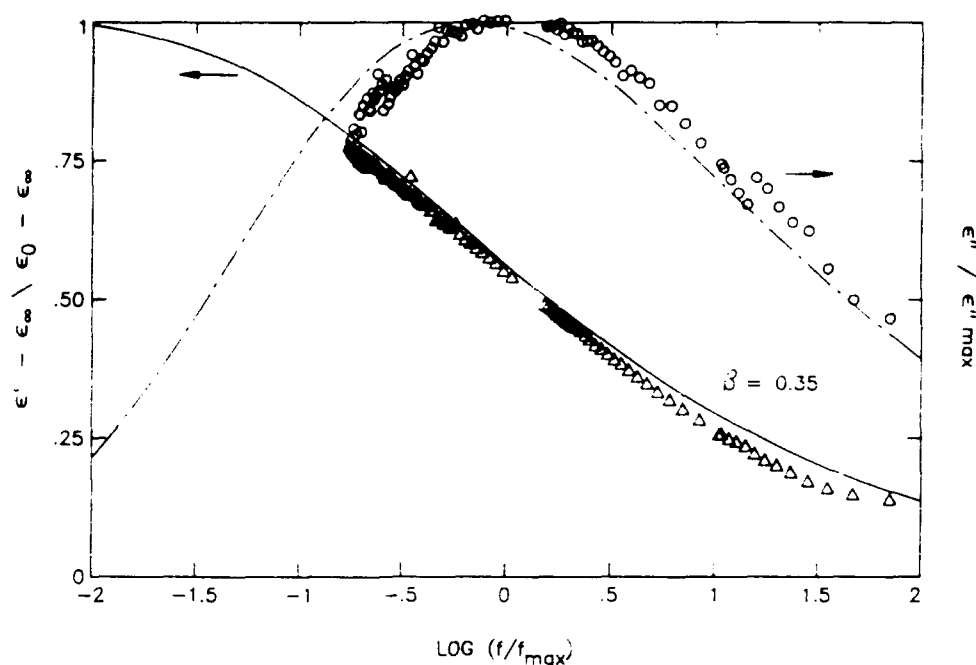


Fig. 12. Normalized dielectric spectrum for chlorobutyl rubber at 294.15 K. System cured with 5 phr ZnO, 6 phr SP1055, 2 phr MBTS, 0.5 phr DPG. Lines represent splines through points calculated from KWW function with $\beta = 0.35$.

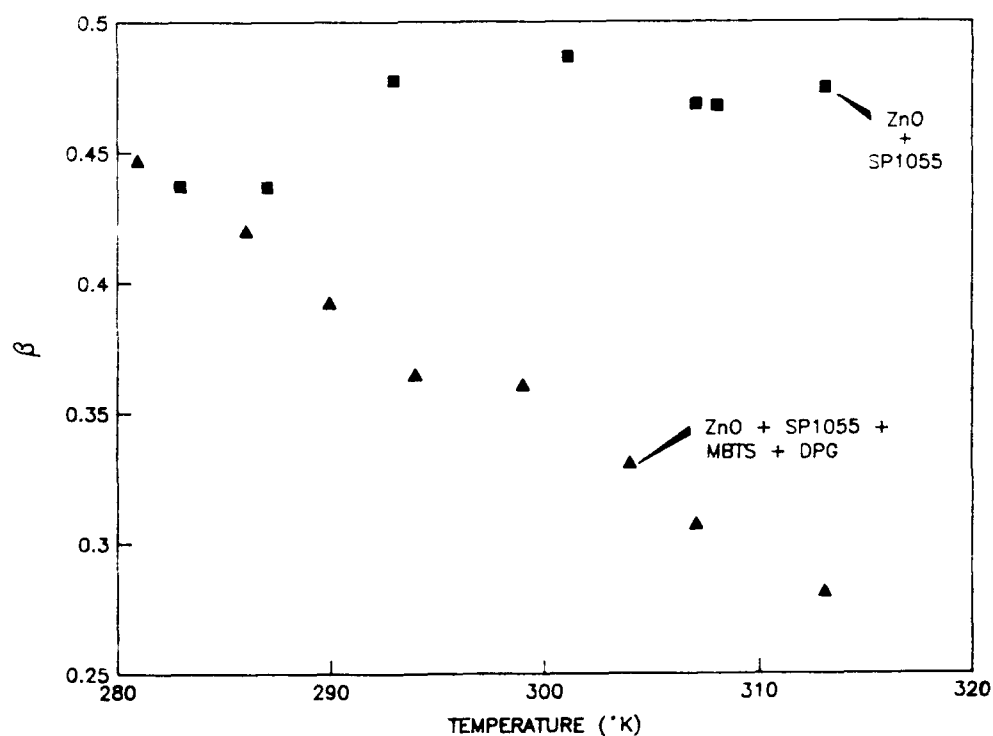


Fig. 13. Effect of temperature on value of exponential factor in KWW function for chlorobutyl rubber with two different cure systems.

DISCUSSION

The primary molecular mechanism involved in both the dielectric and viscoelastic relaxations in these materials is largely an alpha one, with some merging of beta character. Phenomenologically, the polymer networks can be viewed as long-chain molecules that are tied together at certain points by other smaller molecules, perpendicular to the main chains, that have rotatable, permanent dipole moments. These can be perturbed by thermally induced interactions with near neighbors in such a way as to produce a set of oscillators with a distribution of frequencies. The overall effect is one of cooperative relaxation, i.e., thermally induced rotation coupled with main chain segmental motion.

The fit parameter, β , in the KWW function can be viewed as a measure of the variance of the underlying distribution of relaxation times¹⁹. In the present case, the fact that the more complex cure systems have smaller values of β for the dielectric curves can be rationalized on a phenomenological basis by noting that they contain additional types of crosslinks that differ in the rotational energy required, and the polarity of molecules that are contributing to the oscillator strength. In all three cases, stearic acid is also used as a processing aid when the rubber compounds are milled. It is not clear what role, if any, this plays in the dielectric behavior. Some small residual dipolar activity will also be present from butyl zimate and calcium stearate that are used as stabilizers in the butyl and chlorobutyl gums, respectively. The brominated methylol phenol resin-zinc oxide system will form carbon-carbon bonds, and bonds which incorporate the resin between polymer chains. The systems incorporating MBTS and DPG use these as cure accelerators. It is not clear from published literature whether they will also form sulfidic crosslinks, and possibly crosslinks incorporating the amine structure,^{20,21} or accelerator decomposition products that are attached in some manner to the rubber chains. In contrast, the behavior of the zinc oxide-cured system appears to lend support to the formation of carbon-carbon crosslinks in this cure system, rather than carbon-oxygen-carbon crosslinks^{22,23}. These would be expected to show behavior analogous to sulfur cured systems⁸.

It was desired to determine whether the dynamic mechanical data could be related on a molecular level to the observed dielectric behavior, as has been done for other polymers. DeMarzio and Bishop²⁴ have derived relationships between dielectric and mechanical susceptibilities for amorphous polymers. Diaz-Calleja²⁵ derived simple relationships from these for calculating the viscoelastic $\tan \delta$ from dielectric data, and compared experimental data for a number of polymer systems.

The question to be considered here is whether the KWW function is simply an empirical fitting function of such generality that it will fit a large variety of physical phenomena, or if the differences between the fit parameters for the dynamic mechanical and dielectric data for the more complex cure systems can be explained in terms of basic molecular structures and crosslink densities. The crosslink densities, and average values of M_c between crosslinks, were evaluated from the tensile moduli at 100% elongation. As was also evidenced earlier by the Young's moduli shown in Figs. 1 and 2, the crosslink density increases in going from the ZnO cure system to the ZnO, SP1055, MBTS, and DPG cure. The number average molecular weight of segments between crosslinks decreases from approximately 22,000 to 14,000.

The dielectric relaxations are clearly cooperative ones. The dynamic mechanical relaxations are also cooperative, but appear to be influenced more by segmental motions of the main chains. The fit parameter for the

dielectric and dynamic mechanical data are the same for the ZnO cured material, indicating a similar distribution of relaxation times and involvement of similar molecular motions for both processes. The base polymer itself is a random copolymer of polyisobutylene and trans-isoprene, with approximately 2 mole % unsaturation. In the case of the chlorobutyl, it also contains 1.1-1.3 weight % chlorine, existing in the form of approximately 20% tertiary allylic chlorides, and a mixture of isomeric secondary allylic chlorides in approximately equal concentrations²⁰. These will differ in their reactivity, with the tertiary allylic chlorides being most reactive. These are the probable crosslinking sites for the ZnO cure. This system will have the most random distribution of crosslinking sites and largest average molecular weight of polymer between crosslink sites.

Increasing the complexity of the cure system increases both the crosslink density and the types of crosslinks formed. The average molecular weight of polymer between crosslinks will decrease, and the relaxation times for the polymer segments will become more uniform. Thus, the exponent in the KWW function will increase, indicating a more uniform distribution of relaxation times as the rubber becomes more highly crosslinked.

If this is a correct phenomenological explanation of the difference in the KWW fits to the dynamic mechanical behavior of chlorobutyl crosslinked with different curatives, then it is still not clear why the value of the exponent for the system cured with ZnO and SP1055 does not differ from that of the ZnO cured system. Part of the reason for this may be a temperature dependence of the KWW distribution for the rubbers cured with the three different cure systems. This can not be definitively established by the method used here, since shifting the master curves to another reference temperature will simply transpose them along the frequency axis, and have no effect on the KWW fit. All three cure systems were shifted to the same reference temperature, but the temperature dependence of their dynamic mechanical relaxations is different, as shown earlier in the Young's modulus and loss tangent curves of Figs. 1 and 2.

SUMMARY

The temperature and frequency-dependent Young's modulus and loss tangent have been examined as functions of cure systems and plasticizer loading in chemically crosslinked butyl and chlorobutyl rubbers. The crosslinked materials exhibited thermorheologically simple behavior. Dielectric permittivity and loss were measured as functions of frequency and temperature. The viscoelastic and dielectric behaviors were significantly influenced by the type of crosslinking system and by plasticizer loading. The Kolrausch-Williams-Watts "stretched exponential" function was found to be a reasonable fit to both the dielectric and dynamic-mechanical spectra. The effects of molecular motions and cooperative behavior upon the two types of relaxations have been discussed.

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